Synopsis of proposed Ph.D. research work

Title of the proposed thesis:

Synthesis and Structure of Metal-Organic Compounds and Investigation of Various Properties

by

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1. Origin of the research problem: The design, synthesis, characterizations, and applications of metal organic compounds has broadly attracted both scientists and engineers due to the need to understand and control reactions or processes that occur in nanometer-sized spaces. This has a profound commercial impact because solids are widely used as sorbents in important applications such as molecule storage, separation and heterogeneous catalysis.

Historically, zeolites have played a major role in such fields. In contrast to structurally ambiguous materials such as activated carbons and glasses, zeolites are crystalline materials that have a very narrow pore size distributions and important examples of microporous crystalline materials that consists of interconnected tunnels or cages resulting in cavities and pores that are uniform in size for a specific zeolite and thus can be utilized as molecular sieves where molecules small enough to fit into the pores are adsorbed but larger ones are not. The largest pore diameter in a zeolitic material is limited to about 13 Å. Using surfactants as structure directing agents or templates, mesoporous silicate/aluminosilicate materials have been synthesized with pores sizes that are tunable in the range of about 20 to 100 Å. Such materials do not display pores with size uniformity approaching natural zeolites and display non-uniform functionality on their inner surfaces.

Progress in the area of hybrid inorganic-organic materials has lead to the development of coordination compounds that now extend in 1-, 2-, or 3-dimensions. Among the metal organic compounds, metal organic frameworks (MOFs) is a special class in which the backbones or frameworks of these compounds are made by connecting metal ions or metal clusters with organic ligands that when bridging multiple metal centers are commonly referred to as linkers or links.[1] The atomic structure of many MOF can be determined by X-ray crystallography, thus the dimensions of the channels can be determined with excellent certainty. The sizes/shapes are highly tunable, and larger channel sizes can be synthesized when compared to known zeolites.

In the recent years, MOFs has acquired stringent attention owing to their potent application in in gas storage,[2] gas separation,[3] magnetism,[4] catalysis,[5] drug delivery[6] and proton conduction.[7] MOFs possesses several advantages over zeolites and carbon based material as the functional sites can be readily immobolized with in the MOFs.[8] As the luminescence properties of MOFs are very sensitive and depends on their structural characteristics, coordination environment of the metal ions, and their interactions with guest species via coordinate bond, hydrogen bond, π-π interaction etc, MOFs has become an interesting hybrid material for the luminescence based sensing of various analytes.[9] MOFs possesses several advantages over the other luminescence based sensors such as nanomaterials, conjugated polymers, supramolecular polymers, quantum dots etc as their extensive

use is confined due to their multistep processing, stability, harmful system, easy interference from other analytes and lack of molecular organization.[10]

In recent times, the terrorist attack in several countries using explosive has put our daily life in risk. Among the commercially available diverse explosive chemicals, nitroaromatics are extensively used.[11] Nitro aromatics such as 2,4,6-trinitrophenol (TNP), 2,4-dinitro toluene (DNT), 1,3-dinitro benzene (DNB) are commonly act as ingredients for different explosives.[12] In glass, match, fireworks, dye, and lather industries, TNP is extensively used .[13] Besides that, these nitroaromatics has adverse affect on human being.[14] Therefore, the sensing of nitroaromatics is of high significance for both security and environmental pollution control in the present decade.[15]

The very concentration of cadmium, mercury and lead can generate some serious diseases. Several industrial operation, thermometer, batteries, cosmetics, food, leaching from cinnabar, volcanic eruptions are the source of mercury contamination in water.[16] The high affinity of mercury towards the thiol group in enzymes and proteins hampers the normal function of cells and as a consequence many health problem in kidney, brain and central nervous system occurs.[17] Lead is most abandoned among the heavy metals and it has occupied second position among the toxic substances.[18] Batteries, gasoline, lead based paints, industrial pursuits and lead containing connector or goins in pipes are the main source of lead contamination in environment.[19] Lead poisoning affect both adult and children but the lead poisoning in children body is more common. In children body inpaired hearing, decrease of IQs, stunted growth, hypertension and kidney damage can be caused by the very low level of lead poisioning.[20] High level of lead poisoining can put a child in coma and even death.[21] In human body low concentration of cadmium can develop renal dysfunction, calcium metabolism disorder and induce an increased incidence of certain forms of cancer.[22] The excess concentration of Cu^{2+} can generate neurogical problem and generate Wilson's disease, Alzheimer diseases.[23] The deficiency or excess of Fe^{3+} and Fe^{2+} can lead to diseases like Alzheimer's disease, Parkinson's disease, hepatitis and cancer.[24] Aluminium is extensively used in industry. Al^{3+} ions can enter the human body through foods and drinking water.[25] The excess concentration of Al^{3+} in in human body can give the birth of Alzheimer's disease and Parkinson's disease.[26]

F^-, Cl^-, Br^-, CN^-, SO_4^{2-} and PO_4^{3-} plays fundamental roles in environmental and living system.[27] On the other hand, organophosphorous pesticides are extensively used in agriculture and aquaculture to protect the plants and animals from insects, fungi and other pests.[28] They can inhibit he catalytic activity of acetylcholinesterase (AChE) leading to in vivo accumulation of acetylcholine resulting damage in nerve systems and even nerve cell death.[29]

In recent times, in situ and real time characterization of the pH is very much important in the analysis and diagnostics areas because of their prominent advantages.[30] Many diseases can be diagnosed by the changes or abnormalities in the tissue pH, and its treatment could also be monitored by pH measurement.[31] On the other hand, pH controls a large number of industrial processes. In situ and real time pH monitoring in metal etching surface, marine research and aircraft surface[32] have several advantages over classical pH meter, such as small impact on its substrates, fast response and extensive applications.[33]

Therefore, the sensing of the above analytes and pH is of high significance for security, environmental pollution control and human health.

The theories of magnetism and magnetic behavior are abounding in the literature. The validity of some of the theoretical proposals requires model compounds, which are not many. The MOFs can be prepared by careful manipulation of the reactants and such designed MOFs can act as a good model compounds to verify some of the well established theoretical models for the understanding of the magnetic interactions. For example, the presence of infinite – M – O – M – linkages within MOFs either as one – dimensional chains or two – dimensional layers can be used to study and understand the correlation between the structure and the magnetic property.

Magnetic interactions through simple super – exchange interactions leading to ferri and antiferromagnetic behavior in MOFs have been well established.[34] A classic example of a 2D ferromagnet having weak coupling between the layers was established in the cobalt compound, $[Co_2(\mu_3\text{-}OH)(\mu_2\text{-}H_2O)(pyrazine)(OBA)(OBAH)]$ (OBA = 4,4'-oxybis(benzoate).[35] Here the structure consists of Co_4 buterfly clusters connected by pyrazine forming extended 2D layers, which are pillared by the oxy-bisbenzoate anions. The various components are positioned in a body centered arrangement, which is rarely observed in MOF structures. Magnetic kagome lattice based MOF structures have also been reported. Some of these compounds exhibits spin – canted frustration and interesting magnetic behavior.[36] The investigations of this nature provide vital data for the understanding and validation the available magnetic models.

Over the last decade a large number of MOFs have been synthesized in non aqueous medium with various size, shape and used in various kinds of applications.[37] But the collapse of these structure and a loss of crystallinity may occur ones the guest molecules (typically the solvent of synthesis and synthetic components or byproducts) are removed. Besides that these MOFs are also sensitive to air and moisture and they may collapse in open atmosphere and aqueous medium. But for performing many application like sensing, drug delivery, proton conduction, their stability in open atmosphere

and water is highly desirable. So, the synthesis of MOFs in water medium is highly desirable so that it can remain stable in open atmosphere and in aqueous medium. Nevertheless, the synthesis of MOFs in aqueous medium is a challenging work to perform. For this reason, till date very few examples of crystalline MOFs synthesized in water medium with atmospheric and aqueous phase stability have been reported.

2. Objectives of the work:

Against this prior art background, there is still a desire for novel MOFs synthesized in water medium for the application in specific purposes like sensing, magnetism study, proton conduction and other advance applications.

I propose to synthesize new metal organic compounds especially metals organic frameworks in water medium using commercially available ligands such as aromatic carboxylic acids and some simple heterocyclic compounds such as 4,4'-bipyridine, triazole, imidazole etc and to investigate their structures and properties.

(a) To synthesize metal-organic compounds especially metal organic frameworks using aromatic carboxylic acids and organic ligands like 4,4'-bipyridine, triazole, imidazole etc.
(b) To determine the structure of the metal-organic compounds especially metal organic frameworks using powder XRD, single crystal XRD etc.
(c) To characterize the metal-organic compounds especially metal organic frameworks using Thermogravimetric analysis (TGA), Infrared spectroscopy (IR spectroscopy), Scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDX), UV-Visible spectroscopy etc.
(d) To investigate the photoluminescence based sensing properties of the metal-organic compounds especially metal organic frameworks depending on the nature of the metal ions and ligands.
(e) To investigate magnetic property of the metal-organic compounds especially metal organic frameworks depending on the nature of the metal ions and ligands.
(f) To synthesize nanosized oxide using metal-organic compounds especially metal organic frameworks as single source precursor and investigate their relevance properties**.**

3. Methodology:

(a) To synthesize the metal-organic compounds especially metal organic frameworks using slow diffusion method, slow evaporation method and hydrothermal method.

(b) To determine the structure of the metal-organic compounds especially metal organic frameworks using single crystal X-ray diffraction instrument.

(c) To characterize the metal-organic compounds especially metal organic frameworks using PXRD, TGA, IR, SEM, EDX, UV using the respective instruments.

(d) To study the luminescence based sensing property of the metal-organic compounds especially metal organic frameworks using spectrofluorometer.

(e) To study the magnetic property of the metal-organic compounds especially metal organic frameworks using physical properties measurement system (PPMS) and vibrating sample magnetometer (VSM).

4. Future Prospect:

For highly sensitive and selective luminescence sensing, catalysis, gas separation etc using MOFs based on rational control on structure, size, and functional sites within MOFs is important. So, there is huge opportunity for the construction of MOFs with multiple functional sites so that they can be used for the sensing of specific analytes, catalysis and other relevant property study. MOFs could be useful for the sensing of arsenic and other hazardous chemicals in drinking water. Fabrication of nanoscale luminescent MOF into thin films can be used as device for rapid and instant sensing of nitroaromatic explosives in historical places, railway station, airport and other defense sector. Moreover, the synthesis of luminescent MOF in nanoscale is very much promising as they could be used for the application in tissue, in vivo cell imaging for the diagnosis of cancer and tumor and drug delivery monitoring and relevant treatment. For this reason, there is a possibility of pursuing the MOF for the medicinal purpose in the near future.

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